



## Electrochemical behaviour of copper in trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide, an ammonium imide-type room temperature molten salt

K. MURASE, K. NITTA, T. HIRATO and Y. AWAKURA\*

Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

(\*author for correspondence)

Received 1 September 2000; accepted in revised form 29 May 2001

**Key words:** electrodeposition, ionic liquids, nonaqueous solution, redox

### Abstract

The redox behaviour of copper species in an ‘ammonium imide’ room temperature molten salt was examined to clarify the applicability of the salt to the electroplating media of various metals. Trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf<sub>2</sub>N), having an electrochemical window of 5.6 V (50 °C), and the corresponding copper(II) salt were used to prepare the solution. In TMHA-Tf<sub>2</sub>N media the monovalent copper ion, Cu(I), was stable and Cu metal was oxidized, or corroded, in the presence of Cu(II) species as:  $\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+$ . Cathodic electrodeposition of copper metal and its anodic dissolution were, thus one-electron reactions and their current efficiencies were almost 100%.

### 1. Introduction

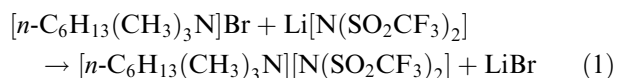
Electrodeposition of metals from aqueous solutions is an important soft process for manufacturing thin-film materials, surface finishing and extractive metallurgy. However, the electrodeposition of base metals, such as zinc, chromium and nickel, from aqueous media is inevitably accompanied by hydrogen evolution, which lowers the cathodic current efficiency of metal deposition. Since the electrodeposition of aluminium, titanium, rare earths and alkaline earths of high quality from aqueous media is actually impossible due to their largely negative redox potentials, nonaqueous media such as aprotic organic solvents and high-temperature molten salts have been employed for the electrodeposition of these metals. Room temperature molten salts (RTMS) [1, 2] or room temperature ionic liquids, have also been developed as promising electrolytes for the electrodeposition of base metals. In this field, chloroaluminates of alkylpyridinium or alkylimidazolium cation have been investigated for aluminium [3] or aluminium alloy [4, 5] electroplating media. To avoid high hygroscopicity arising from the use of aluminium chloride, however, attempts have been made to combine the alkylimidazolium cations with fluorine-containing hydrophobic anions, for example, BF<sub>4</sub><sup>−</sup> [6], CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> (TfO<sup>−</sup>) [7], (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>−</sup> (Tf<sub>2</sub>N<sup>−</sup>) [8], and H(HF)<sub>*n*</sub><sup>−</sup> ions [9], and investigated for electrodeposition media [10]. Recently, a new series of RTMS consisting of tetraalkylammonium cations and Tf<sub>2</sub>N<sup>−</sup> anion, sometimes abbreviated as

TFSI<sup>−</sup> anion, was found independently by MacFarlane et al. [11, 12] and Matsumoto et al. [13]. This type of RTMS, which is commonly named an ‘ammonium-imide’ salt, has a wide electrochemical window of about 5 V and, thus, the RTMS is suited to practical application as a solvent for the electrodeposition process. In this paper we report the electrochemical behaviour of copper species in an ammonium-imide RTMS, trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf<sub>2</sub>N).

### 2. Experimental details

#### 2.1. Preparation of molten salt

The TMHA-Tf<sub>2</sub>N salt, [*n*-C<sub>6</sub>H<sub>13</sub>(CH<sub>3</sub>)<sub>3</sub>N][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>], was synthesized in the atmosphere by the reaction of trimethyl-*n*-hexylammonium bromide (Tokyo Kasei Kogyo), [*n*-C<sub>6</sub>H<sub>13</sub>(CH<sub>3</sub>)<sub>3</sub>N]Br, with lithium bis((trifluoromethyl)sulfonyl)amide (Fluka), Li[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>], as

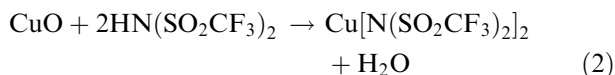


50.00 g (0.224 mol) of [*n*-C<sub>6</sub>H<sub>13</sub>(CH<sub>3</sub>)<sub>3</sub>N]Br and 64.02 g (0.224 mol) of Li[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] were weighed and each was dissolved in 100 cm<sup>3</sup> of deionized water. The chemicals were of reagent grade and used without pretreatment; the deionized water used to dissolve the

chemicals had a specific resistance larger than  $5 \times 10^6 \Omega \text{ cm}$ . The two aqueous solutions were mixed and agitated with a magnetic stirring unit for 1 h at 70 °C. According to the above reaction, TMHA-Tf<sub>2</sub>N salt was formed and separated from the aqueous phase as an organic phase. To extract the TMHA-Tf<sub>2</sub>N salt completely from the aqueous phase, 100 cm<sup>3</sup> of dichloroethane was added and stirred for 1 h at room temperature. The organic phase (i.e., lower layer) was then separated using a separating funnel. The dichloroethane solution of TMHA-Tf<sub>2</sub>N salt was washed with 100 cm<sup>3</sup> of deionized water three times in order to remove residual LiBr. The complete removal of Br<sup>-</sup> ion was ascertained by addition of a AgNO<sub>3</sub> aqueous solution to the washings; if Br<sup>-</sup> remains, an insoluble AgBr forms. The dichloroethane was then distilled off using a rotating evaporator and the resulting crude TMHA-Tf<sub>2</sub>N salt was dried in a vacuum desiccator at 120 °C for more than three days. The transparent colorless TMHA-Tf<sub>2</sub>N salt was transferred into a glove box, in which further electrolytic experiments were carried out. The TMHA-Tf<sub>2</sub>N salt obtained has a melting point ~27 °C and was identified by elemental analysis at the Center for Organic Elemental Microanalysis of Kyoto University as C 31.02% (31.13%), H 5.16% (5.22%), N 6.57% (6.60%), F 27.18% (26.86%) (calculated values are in parentheses); the contents of oxygen and sulfur could not be analysed because the TMHA-Tf<sub>2</sub>N contains fluorine.

## 2.2. Preparation of copper(II) salt

To investigate the electrochemical properties of copper ions in the molten salt, copper(II) salt with the common anion, Tf<sub>2</sub>N<sup>-</sup>, was prepared as follows. 5.00 g (17.8 mmol) of bis((trifluoromethyl)sulfonyl)amine (Fluka), HN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, was weighted and dissolved in 100 cm<sup>3</sup> of deionized water. The aqueous solution was added dropwise over 1 h to another 100 cm<sup>3</sup> of deionized water suspended with 0.70 g (8.8 mmol) of copper(II) oxide (Nacalai tesque), CuO, under stirring; the mixture was allowed to react for 2 h at 70 °C as



Unreacted CuO was then filtered off and the water was distilled off, yielding a blue-coloured hydrated salt, Cu(Tf<sub>2</sub>N)<sub>2</sub> · xH<sub>2</sub>O. This hydrated salt was heated *in vacuo* at 120 °C for more than three days and the resulting greenish anhydrous Cu(Tf<sub>2</sub>N)<sub>2</sub> was transferred into a glove box. The microanalysis of the resulting Cu(Tf<sub>2</sub>N)<sub>2</sub> to check the removal of water was not carried out, since the contents of oxygen and sulfur could not be analyzed (see the preceding section).

## 2.3. Electrochemical measurements

Preparation of sample solutions (e.g., Cu(Tf<sub>2</sub>N)<sub>2</sub> solution of TMHA-Tf<sub>2</sub>N salt) and all electrolytic experi-

ments, that is, cyclic voltammetry and cathodic bulk electrodeposition, were carried out in an argon filled glove box equipped with a molecular-sieve gas purification system. The water content of the glove box was less than 5 ppm. The electrolytic experiments were performed using a conventional three electrode set-up comprising a potentiostat connected to a function generator and a coulometer. Cyclic voltammograms were taken by scanning the potential of the working electrode at a constant scan rate of 100 mV s<sup>-1</sup>. Four types of electrode were employed for the working and/or counter electrodes: Pt sheet 1 (4 mm × 4 mm), Pt sheet 2 (15 mm × 15 mm), glassy carbon (GC) rod (dia. 3 mm) cemented in a resin, and oxygen free Cu sheet (10 mm × 85 mm); the detailed combination of the electrodes is shown with the results. The Pt and Cu sheets were washed with dilute nitric acid before use. The surface of the GC electrode was polished with 1 μm and 0.25 μm diamond abrasives. An I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrode consisting of Pt wire immersed in TMHA-Tf<sub>2</sub>N solution of 15 mM I<sub>2</sub> and 60 mM (*n*-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NI (M ≡ mol dm<sup>-3</sup>), contained in a glass tube with ceramic frit at the bottom, was used as a reference. The electrode potential was checked by cyclic voltammogram for TMHA-Tf<sub>2</sub>N containing 10 mM ferrocene. A glass vessel (capacity 20 cm<sup>3</sup>) was used as the electrolytic cell. The electrolytic solution was agitated with a magnetic stirring unit. To keep the temperature of the solution at 50 °C for all runs, the electrolytic cell was placed in a double-walled glass heating jacket in which warm water of 50 °C was circulated from outside the glove box.

Copper deposits on the cathode were identified by X-ray diffractometry (XRD) using a molybdenum X-ray tube ( $\lambda = 70.926 \text{ pm}$ ). The current efficiency for copper deposition was calculated as  $Q_{\text{Cu}}/Q_{\text{total}}$ , where  $Q_{\text{Cu}}$  is the charge estimated from a deposited mass of Cu whose deposition is assumed to be one- or two-electron reduction (see Section 3).  $Q_{\text{total}}$  is the total quantity of charge passed during the electrodeposition.

## 3. Results and discussion

### 3.1. Electrochemical window of TMHA-Tf<sub>2</sub>N

MacFarlane et al. reported that ammonium-imide salts exhibit a large electrochemical window of >4.5 V, which is wider than that of alkylimidazolium bis((trifluoromethyl)sulfonyl)amide salts [11, 12]. A cyclic voltammogram was undertaken to obtain the window of pure TMHA-Tf<sub>2</sub>N salt prepared in the present study. Pt sheets 1 or GC electrodes were used for the working and counter electrodes. The rest potentials of the Pt and GC electrodes were +0.48 and +0.38 V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup>, respectively. The voltammogram was taken by scanning the potential of the working cathodically first to -3.50 V and then anodically to +3.00 V. In the case of Pt electrodes (Figure 1), steep onsets of cathodic and anodic currents appeared at -3.0 and +2.6 V, respec-

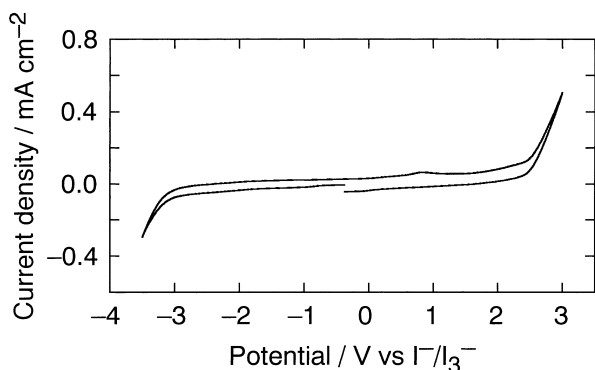


Fig. 1. Cyclic voltammogram for pure TMHA-Tf<sub>2</sub>N salt at 50 °C. Working and counter electrodes, platinum sheet. Sweep rate 100 mV s<sup>-1</sup>.

tively due to the reductive and oxidative decomposition of the salt. A weak anodic wave at +0.8 V was associated with the oxidation of a cathodic decomposition product, since the wave appeared only after scanning the potential beyond -3.0 V (cf. Figure 4(a)). The electrochemical window of TMHA-Tf<sub>2</sub>N was thus about 5.6 V and 50 °C. In the case of GC electrodes, the cathodic and anodic limits of the electrochemical window were recognized at -3.2 and +2.6 V. The window for GC electrodes was slightly wider than that for Pt; this may have been due to a lower electrocatalytic action of carbon against cathodic decomposition of organic TMHA-Tf<sub>2</sub>N salt.

It is well known that the redox potential of ferrocene/ferricinium ion (Fc/Fc<sup>+</sup>) system is little affected by the solvent and, therefore, IUPAC recommended measuring Fc/Fc<sup>+</sup> redox in order to compare particular potential data with others [14]. A cyclic voltammogram for TMHA-Tf<sub>2</sub>N containing 10 mM ferrocene (Figure 2) gave a pair of Fc/Fc<sup>+</sup> redox waves at  $E_c = +0.07$  V and  $E_a = +0.24$  V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup>. The anodic peak current ( $|i_a| = 2.6$  mA cm<sup>-2</sup>) was almost equal to the cathodic one ( $|i_c| = 2.4$  mA cm<sup>-2</sup>), suggesting that the Fc/Fc<sup>+</sup> redox in TMHA-Tf<sub>2</sub>N is reversible as is often the case

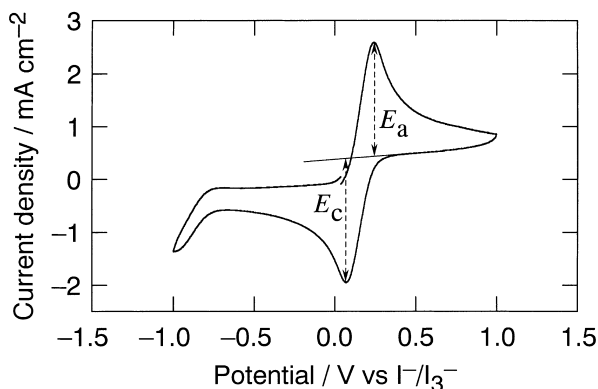


Fig. 2. Cyclic voltammogram for TMHA-Tf<sub>2</sub>N salt containing 10 mmol dm<sup>-3</sup> ferrocene at 50 °C. Working and counter electrodes, glassy carbon. Sweep rate 100 mV s<sup>-1</sup>. Ferrocene/ferricinium couple had a potential of +0.16 V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup> couple in TMHA-Tf<sub>2</sub>N salt.

for other nonaqueous solvents. However, their peak separation of 0.17 V ( $= E_a - E_c$ ) was larger than the ideal for one-electron redox (i.e., 0.06 V). This may be due to IR drop arising from the relatively low conductivity of the TMHA-Tf<sub>2</sub>N solution, but the effect of conductivity was not considered in the present work.

According to the voltammogram, the redox potential of Fc/Fc<sup>+</sup> in TMHA-Tf<sub>2</sub>N was +0.16 V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup>. Therefore, the cathodic and anodic limits of the TMHA-Tf<sub>2</sub>N salt were -2.9 and +2.7 V vs Fc/Fc<sup>+</sup>, respectively. The electrochemical windows reported for other nonaqueous solvents [15] are summarized in Figure 3, together with that of TMHA-Tf<sub>2</sub>N salt. Although TMHA-Tf<sub>2</sub>N has a wide electrochemical window, the cathodic limit is not as negative as for conventional aprotic solvents (e.g., acetonitrile (AN), dimethyl sulfoxide (DMSO) and propylene carbonate (PC)). From the standpoint of the electrochemical window, TMHA-Tf<sub>2</sub>N does not appear suitable for cathodic electrodeposition of metals compared to the above aprotic solvents. In view of the high solubility of metals salts to RTMS, however, TMHA-Tf<sub>2</sub>N may well also be an appropriate cathodic metal deposition medium. In contrast, TMHA-Tf<sub>2</sub>N has a higher resistance against anodic decomposition than a number of aprotic solvents. The anodic resistivity is attributed to a tetraalkylammonium cation.

### 3.2. Electrodeposition of copper from Cu(II) in TMHA-Tf<sub>2</sub>N

Figure 4 depicts cyclic voltammograms for TMHA-Tf<sub>2</sub>N with or without Cu(II) ion, that is, Cu(Tf<sub>2</sub>N)<sub>2</sub>. The working and counter electrodes were Pt sheet 1 and Cu sheet, respectively. In the presence of Cu(II), three cathodic waves were recognized at around +0.6, 0.0 and -1.3 V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup> and the peak current of the waves increased with an increase in the amount of Cu(Tf<sub>2</sub>N)<sub>2</sub> added. In view of the Fc/Fc<sup>+</sup> redox appearing at +0.16 V (Figure 2), however, the peak at relatively low potential -1.3 V was not attributed to a redox of noble copper species but to some impurity, probably H<sub>2</sub>O. The remaining two waves at +0.6 and 0.0 V correspond to the redox of copper as discussed later. Corresponding to these cathodic waves, three anodic waves were observed at +1.3, +0.5 and -0.7 V, respectively.

Potentiostatic bulk electrolysis was carried out at potentials in the range 0.0 to -1.2 V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup> using 0.01 M Cu(II) solution. Table 1 summarizes the features of the deposits. Electrolysis for 24 h at -1.2 V gave no deposit on the Pt sheet (i.e., cathode substrate) while powdery black particles appeared in the solution. The powdery deposits were also obtained at -1.0, -0.8 and -0.4 V, both on the cathode and in the solution bulk. At these potentials the deposit morphology was dendritic and did not adhere to the substrate. On the other hand, adhesive deposits were obtained at higher cathode potentials, or lower cathodic overpotentials, without the

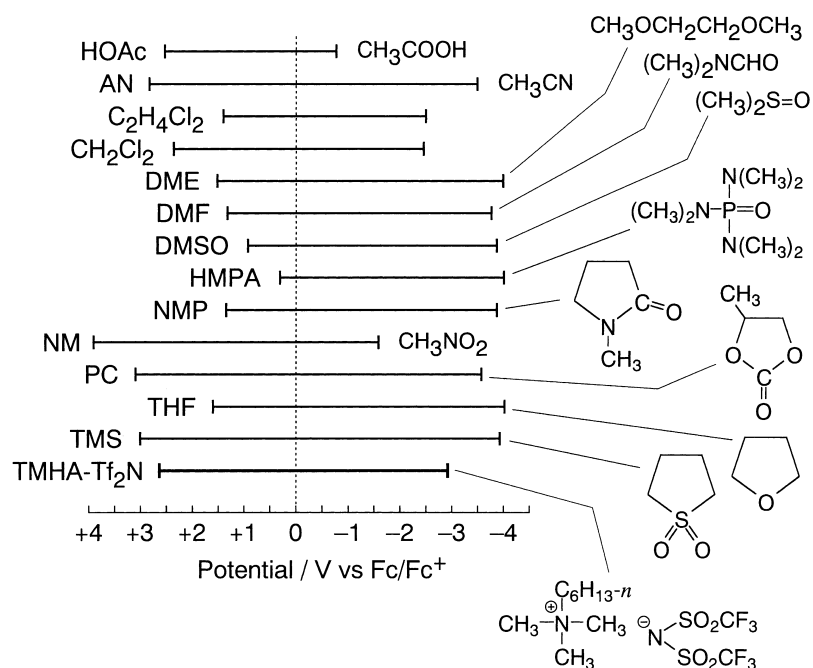


Fig. 3. Comparison of electrochemical window of TMHA-Tf<sub>2</sub>N salt with those of nonaqueous solvents. Data for nonaqueous solvents were taken from reference [15]. Potential was recalculated for ferrocene/ferricinium (Fc/Fc<sup>+</sup>) redox couple. AN: acetonitrile; DME: 1,2-dimethoxyethane; DMF: dimethyl formamide; DMSO: dimethyl sulfoxide; HMPA: hexamethylphosphoric triamide; NMP: *N*-methyl-2-pyrrolidone; NM: nitromethane; PC: propylene carbonate; THF: tetrahydrofuran; TMS: tetramethylene sulfone (sulfolane); TMHA-Tf<sub>2</sub>N: trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide.

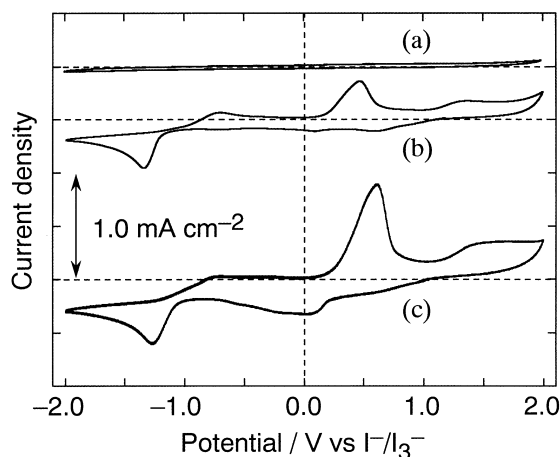


Fig. 4. Cyclic voltammogram for TMHA-Tf<sub>2</sub>N salt containing (a) 0.00 M, (b) 0.01 M, and (c) 0.02 M of Cu(Tf<sub>2</sub>N)<sub>2</sub> at 50 °C. Working and counter electrodes were platinum and copper sheets respectively. Sweep rate 100 mV s<sup>-1</sup>.

formation of black particles in the solution. Electrolysis at -0.1 V resulted in brown-black deposits without metallic luster. Further, a deposit with metallic luster was electrodeposited at 0.0 V. Figure 5 shows the X-ray diffraction pattern of the deposit obtained at 0.0 V on Pt sheet 2. Diffractions due to copper metal appeared at  $2\theta$  of 19.6°, 22.7°, 32.3° and 38.0° in addition to those from Pt substrate.

Table 1. Feature of deposits obtained by potentiostatic electrolysis of TMHA-Tf<sub>2</sub>N salt containing 0.01 mol dm<sup>-3</sup> Cu(Tf<sub>2</sub>N)<sub>2</sub>

Cathode potential/V	Feature	
	On Pt cathode	In bulk solution
-1.2	no deposit	black powder
-1.0	black powder	black powder
-0.8	black powder	black powder
-0.4	black film	black powder
-0.1	brown-black film	no deposit
0.0*	brown metallic film	no deposit

\* 0.04 mol dm<sup>-3</sup> Cu(Tf<sub>2</sub>N)<sub>2</sub>.

The current efficiency for copper deposition from 0.02 M Cu(II) solution at 0.0 V vs I<sup>-</sup>/I<sub>3</sub><sup>-</sup> was estimated. The total quantity of charge passed during the electrodeposition was 15.3 C; deposited copper on the Pt cathode and dissolved copper from Cu anode were 18.7 and 22.8 mg, respectively. Assuming that the cathodic deposition and the anodic dissolution of copper were both two-electron reactions ( $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ ), their current efficiencies were calculated at 185 and 226% respectively. This suggests that the copper deposition and dissolution involved one-electron redox reactions. In other words, monovalent Cu(I) was formed spontaneously in the solution without electrolysis, whereas only divalent copper ions were initially dissolved to TMHA-Tf<sub>2</sub>N salt.

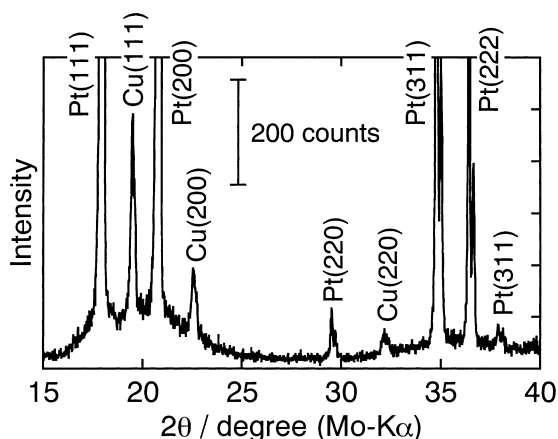


Fig. 5. X-ray diffraction pattern for deposit on platinum sheet. Deposition was carried out under potentiostatic condition at 0.0 V vs  $I^-/I_3^-$  at 50 °C using TMHA- $Tf_2N$  salt containing 0.04 M  $Cu(Tf_2N)_2$ .

### 3.3. Dissolution of copper metal in the presence of $Cu(II)$

To investigate the spontaneous formation of  $Cu(I)$  species, a copper metal electrode was immersed in 5 cm<sup>3</sup> of TMHA- $Tf_2N$  (50 °C) containing 0.02 M, that is, 6.4 mg, of  $Cu(II)$ . It was found that the mass of the copper electrode decreased with time and, at the same time, the light green colour of the solution due to  $Cu(II)$  ions became paler, indicating the formation of colourless  $Cu(I)$  ions as  $Cu^{2+} + Cu \rightarrow 2Cu^+$ . The weight loss of the copper electrode as a function of the immersion time is shown in Figure 6. The reaction came to equilibrium after 72 h immersion and further dissolution of copper metal did not take place. Under the equilibrium, the solution still assumed a pale green colour, suggesting the presence of minute quantities of unreacted divalent  $Cu(II)$ . The final weight loss of copper metal was 3.8 mg, indicating that 60% of  $Cu(II)$  ions reacted with copper metal.

In consequence, copper metal was dissolved, or corroded, in the presence of  $Cu(II)$  ions, yielding monovalent copper species. Divalent copper ion and copper metal in TMHA- $Tf_2N$  salt can be used as oxidizing and reducing agents, respectively. Such a high

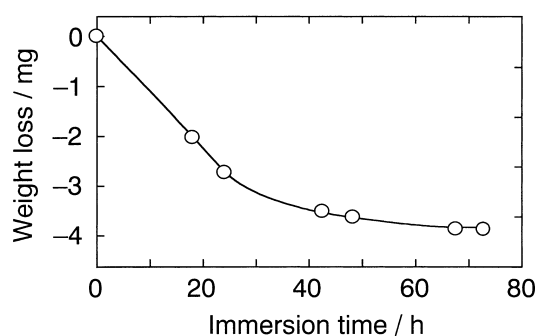


Fig. 6. Variation of the weight of copper metal sheet immersed in TMHA- $Tf_2N$  salt containing 0.02 M  $Cu(Tf_2N)_2$  at 50 °C.

stability of  $Cu(I)$  species in RTMSs has also been reported for chloroaluminates [16] and tetrafluoroborate [10] based melts.

### 3.4. Electrodeposition of copper from $Cu(I)$ in TMHA- $Tf_2N$

Three solutions with different concentrations of  $Cu(I)$  species were prepared by changing the immersion time of Cu metal into 0.02 M  $Cu(II)$  solution: 0 h (solution 1), 24 h (solution 2), and 72 h (solution 3). Table 2 summarizes the concentrations of  $Cu(II)$  and  $Cu(I)$  species estimated from the weight loss of the Cu metal. The predominant copper species in solutions 1 and 3 were  $Cu(II)$  and  $Cu(I)$ , respectively, while solutions 2 contained both species equally. Figure 7 shows cyclic voltammograms for the three solutions; Pt sheet 1 and Cu sheet were used for the working and counter electrodes, respectively. The rest potential of the Pt working decreased with increasing  $Cu(I)$  ions, the reductant. Two cathodic waves in the range from +1.0 to -1.0 V vs  $I^-/I_3^-$  and two anodic waves in the range

Table 2. Solutions with different concentration of  $Cu(I)$  species prepared by changing the immersion time of copper metal into 0.02 mol dm<sup>-3</sup>  $Cu(II)$  solution

Solution	Immersion time/h	Concentration*/mmol dm <sup>-3</sup>	
		$Cu(II)$	$Cu(I)$
1	0	20	0
2	24	12	16
3	72	8	24

\* Concentration of copper ionic species estimated from the weight loss of copper metal.

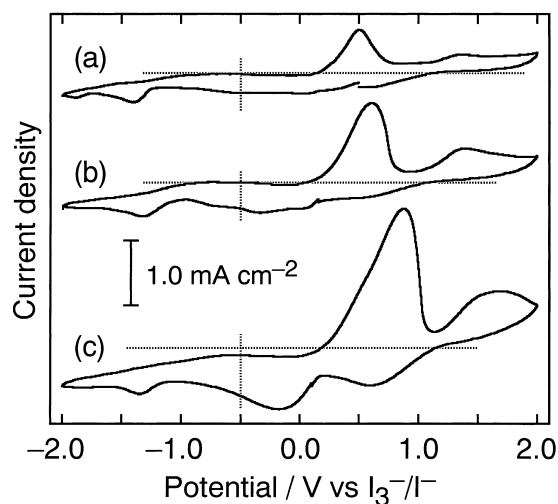


Fig. 7. Cyclic voltammogram for TMHA- $Tf_2N$  salt containing  $Cu(I)$  species: (a) solution 1, (b) solution 2, and (c) solution 3 (Table 2) at 50 °C, prepared by changing the immersion time of Cu metal into 0.02 M  $Cu(II)$  solution (see text). Working and counter electrodes were platinum and copper sheets, respectively. Sweep rate 100 mV s<sup>-1</sup>.

from +0.5 to 2.0 V became clear and intense with increasing Cu(I) content. According to the results of bulk electrodeposition, the cathodic peak at  $-0.2$  V, in the case of solution 3, was attributed to the metal deposition as:  $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$ , while that at  $+0.6$  V was  $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$ . Therefore, it seems reasonable to consider that the two anodic waves peaking at  $+0.9$  and  $+1.7$  V corresponded to the reverse processes:  $\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^-$  and  $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{e}^-$ .

Bulk electrodeposition from solution 3, saturated with Cu(I) ions, was carried out at  $0.2 \text{ mA cm}^{-2}$  using Pt sheet 1 cathode and copper sheet anode. After the electrolysis with a total quantity of charge of  $16.69 \text{ C}$ , the weight gain of the cathode and loss of the anode were  $10.7$  and  $11.1 \text{ mg}$ , respectively. These correspond to the current efficiency of  $97$  and  $101\%$  and substantiated that the copper deposition and dissolution proceeded under a one-electron redox reaction.

#### 4. Conclusion

In this work, the redox behaviour of copper species in an 'ammonium imide' room temperature molten salt was demonstrated in order to clarify the applicability of the salt to the electroplating media of various metals. Trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf<sub>2</sub>N), having an electrochemical window of  $5.6 \text{ V}$  ( $50^\circ\text{C}$ ), and the corresponding copper(II) salt were synthesized. In TMHA-Tf<sub>2</sub>N media the monovalent copper ion, Cu(I), was stable and Cu metal was oxidized, or corroded, by Cu(II) species. Cathodic electrodeposition of copper metal and anodic dissolution of it were, thus, one-electron reactions and their current efficiencies were almost  $100\%$ . Electrodeposition of other metals such as Zn, Ni, and rare earths is now under investigation.

#### Acknowledgement

This work was supported by Grant-in-Aid for Scientific Research (no. 12 650 733) from the Japan Society for the Promotion of Science. The financial support of The Kawakami Memorial Foundation is also acknowledged.

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